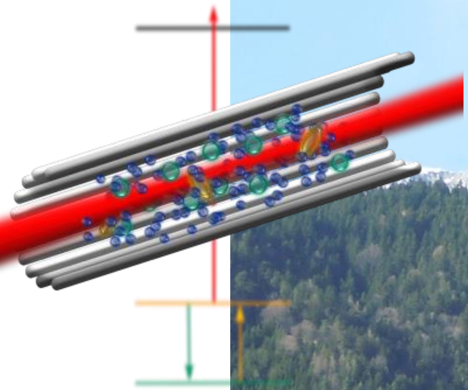
Molecular Systems

Bound-free and bound-bound spectroscopy of cold trapped molecular ions



Roland Wester

71st International Symposium on Molecular Spectroscopy

Urbana-Champaign

June 21, 2016

Institut für Ionenphysik und Angewandte Physik
Universität Innsbruck
Austria

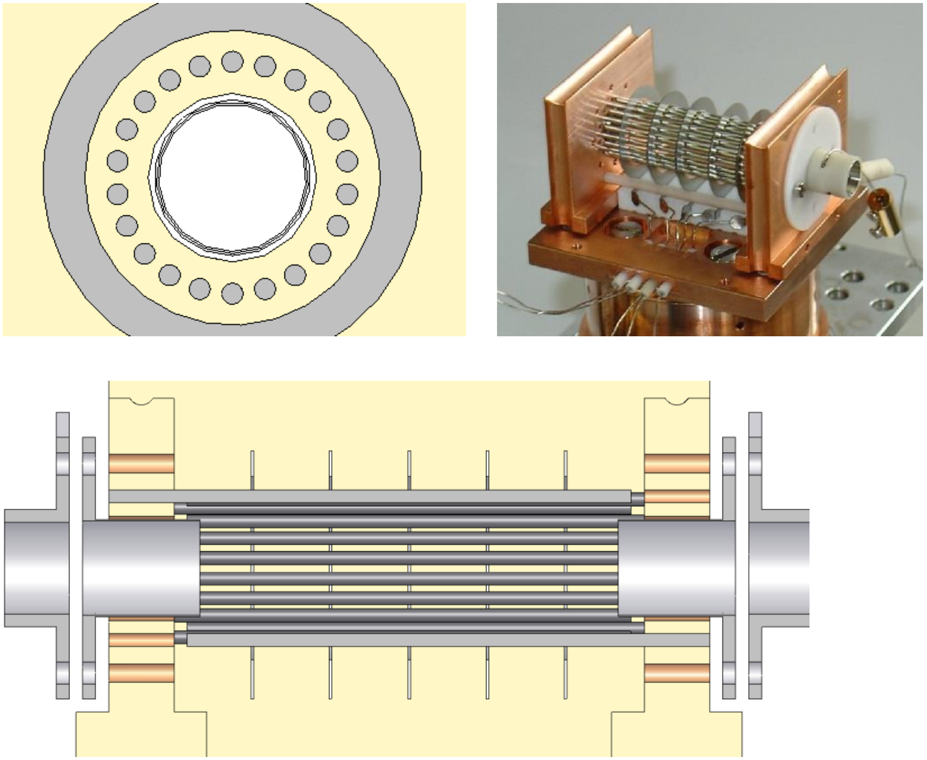
Outline

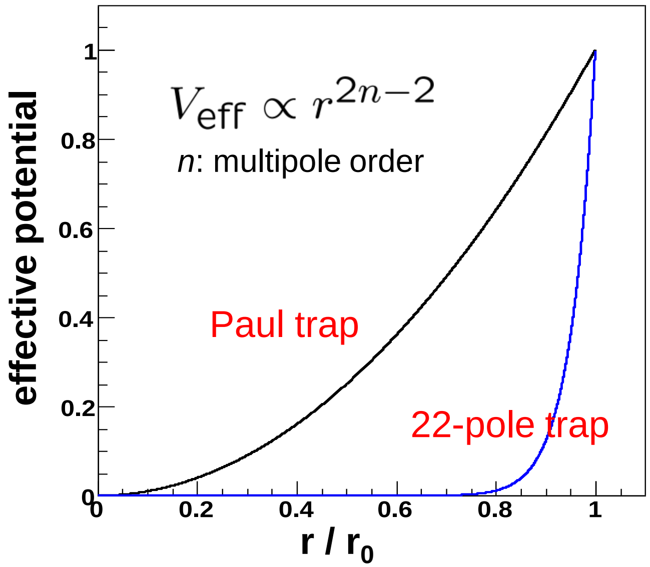
- Spectroscopy in multipole rf ion traps
- Vibrational overtone transitions
- Bound-free photodetachment spectroscopy
- Terahertz rotational spectroscopy
- Electronic spectra of the Atkins‘ snowball

Multipole rf ion traps

The 22-pole ion trap

Dieter Gerlich, Physica Scripta (1995)

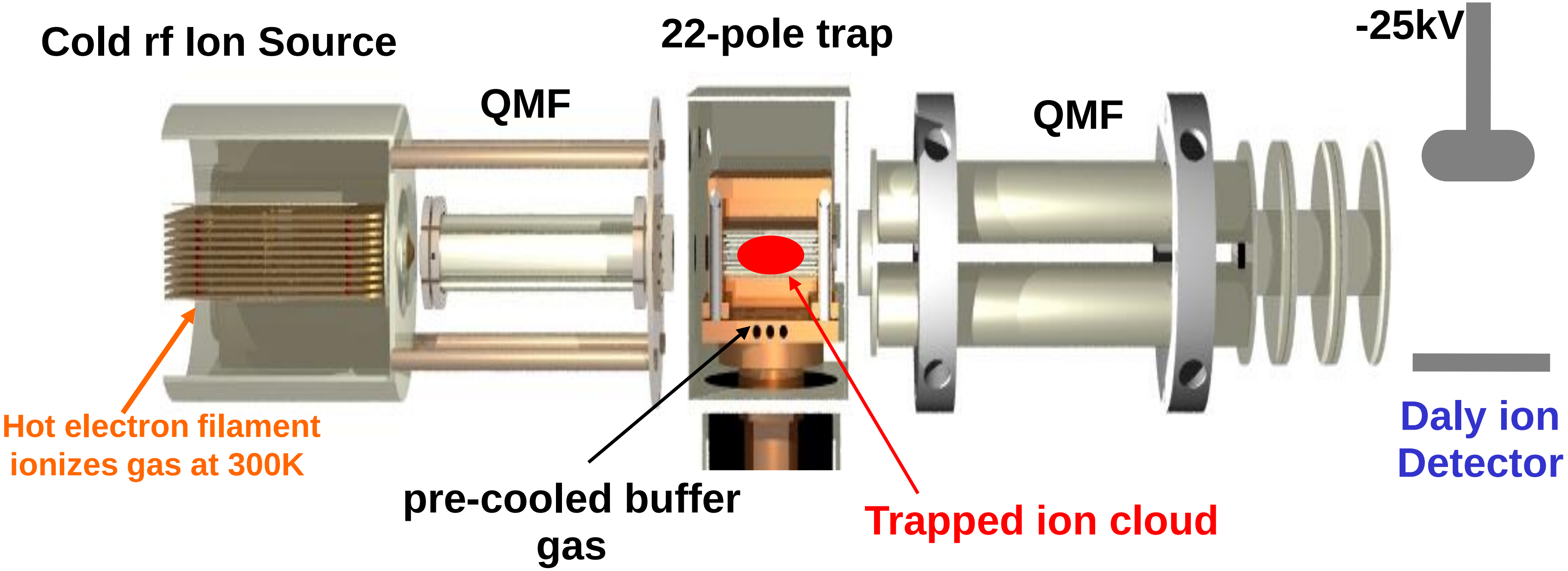




- Large almost field free volume
- Variable temperature 8-300 K
- Buffer gas cooling of internal and translational motion
- Neutral reactants @ well defined density

RW, J. Phys. B (2009)

22-pole trap setup based on rf mass spectrometers



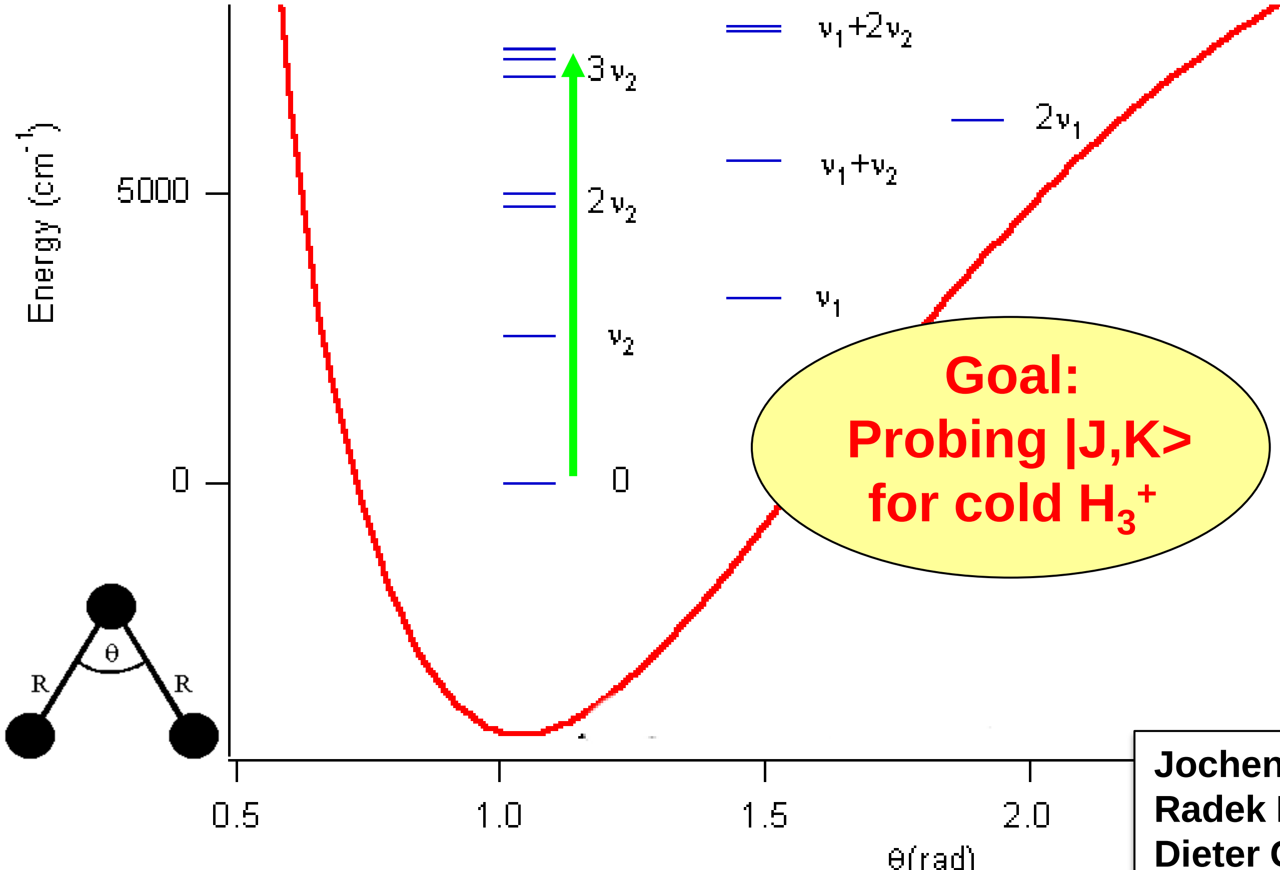
“Classical“ 22-pole trap setup by D. Gerlich et al.

Spectroscopy by laser-induced reactions

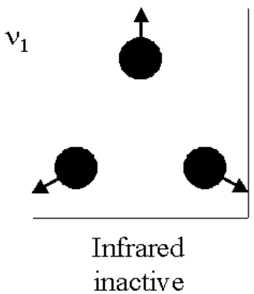
$AB^+(v,J) + X + h\nu \longrightarrow$ new products

Spectroscopy of H_3^+ by laser-induced reactions

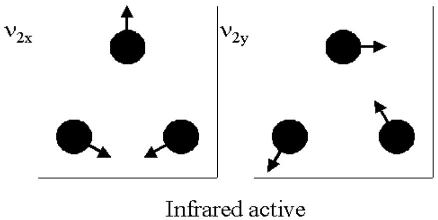
Vibrational levels of H_3^+



breathing mode



degenerate bending modes

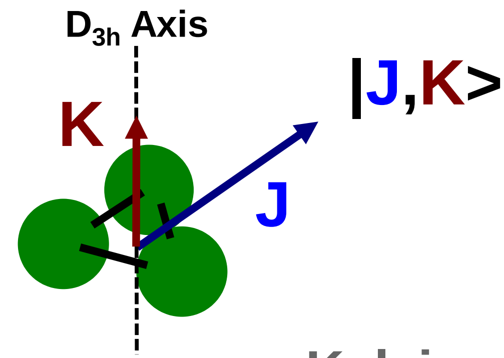


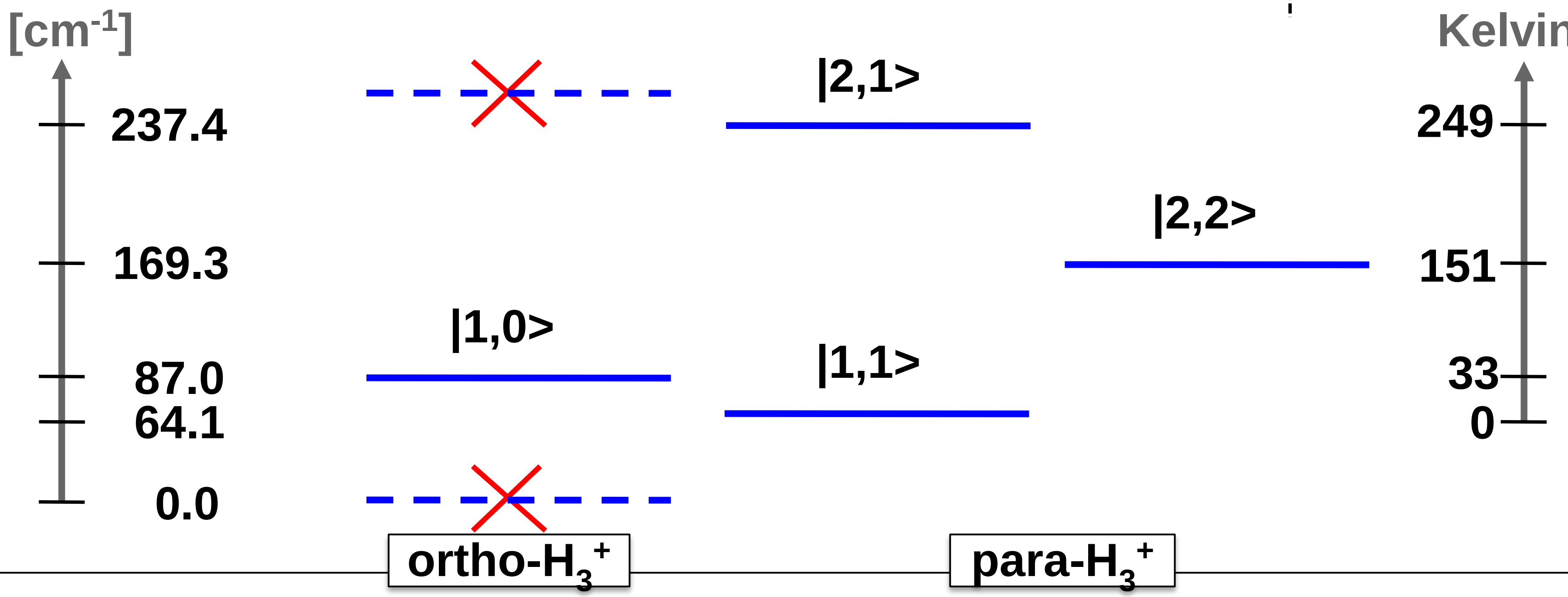
Jochen Mikosch, Holger Kreckel, Radek Plasil, Juraj Glosik, Dieter Gerlich, Andreas Wolf, Dirk Schwalm, RW, J. Chem. Phys. (2004)

Spectroscopy of H_3^+ by laser-induced reactions

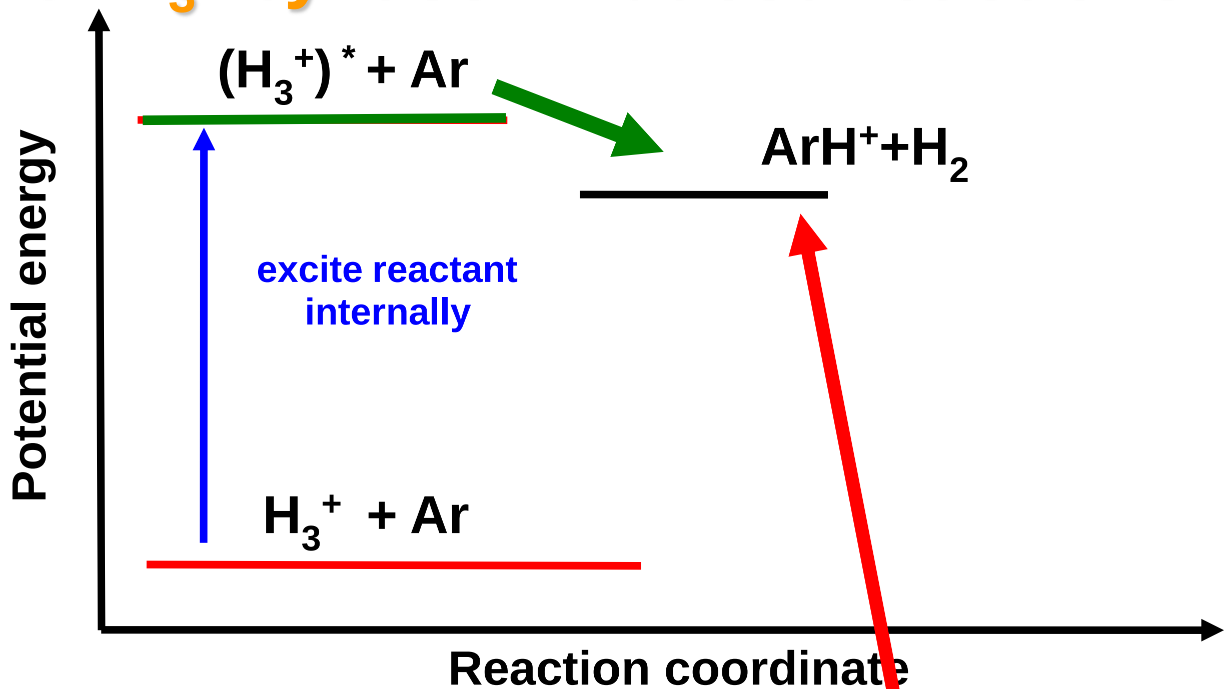
The lowest rotational states

$$E_{rot} = \hbar^2 \frac{J(J+1)}{2 I_\perp} + \frac{K^2 \hbar^2}{2}\left(\frac{1}{I_\parallel} - \frac{1}{I_\perp}\right)$$





Spectroscopy of H_3^+ by laser-induced reactions



$H_3^+ (v_2=0) + Ar \rightleftarrows ArH^+ + H_2$ (- 0.57 eV)

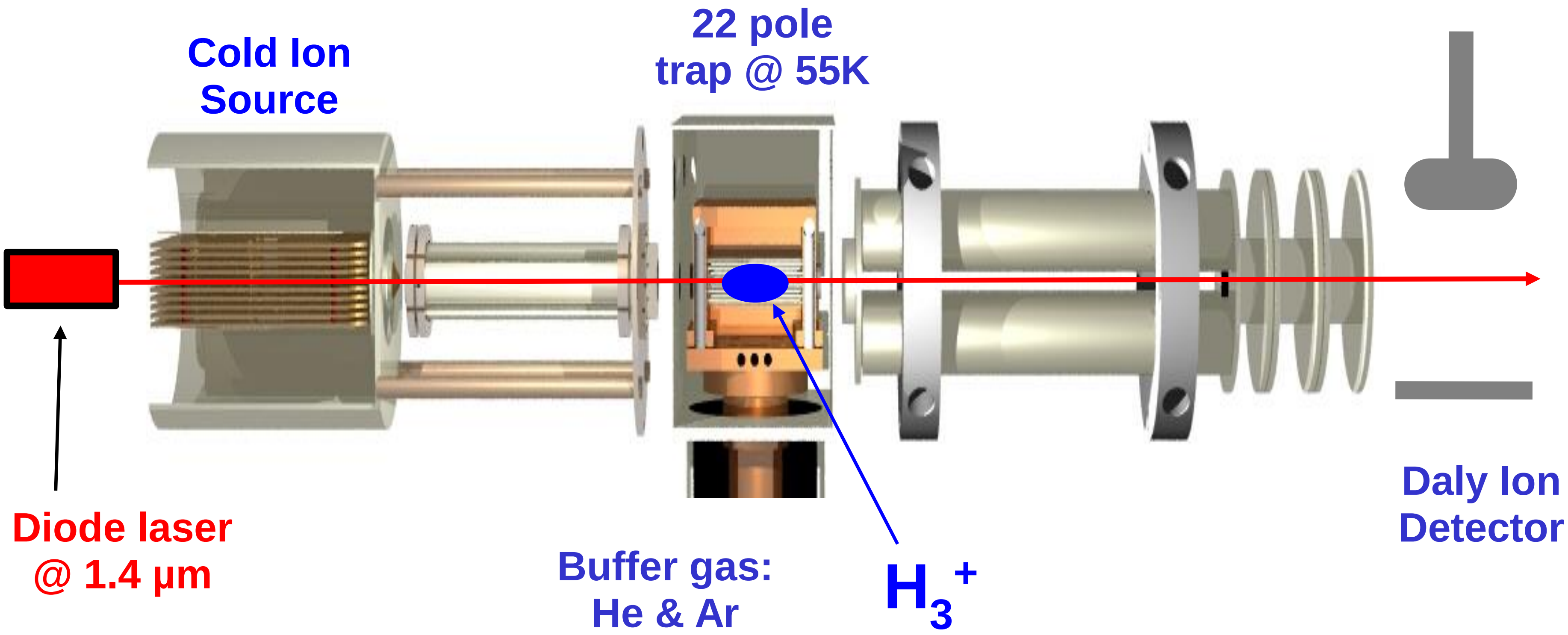
$H_3^+ (v_2=1) + Ar \rightleftarrows ArH^+ + H_2$ (- 0.26 eV)

$H_3^+ (v_2=2) + Ar \rightleftarrows ArH^+ + H_2$ (+ 0.05 eV)

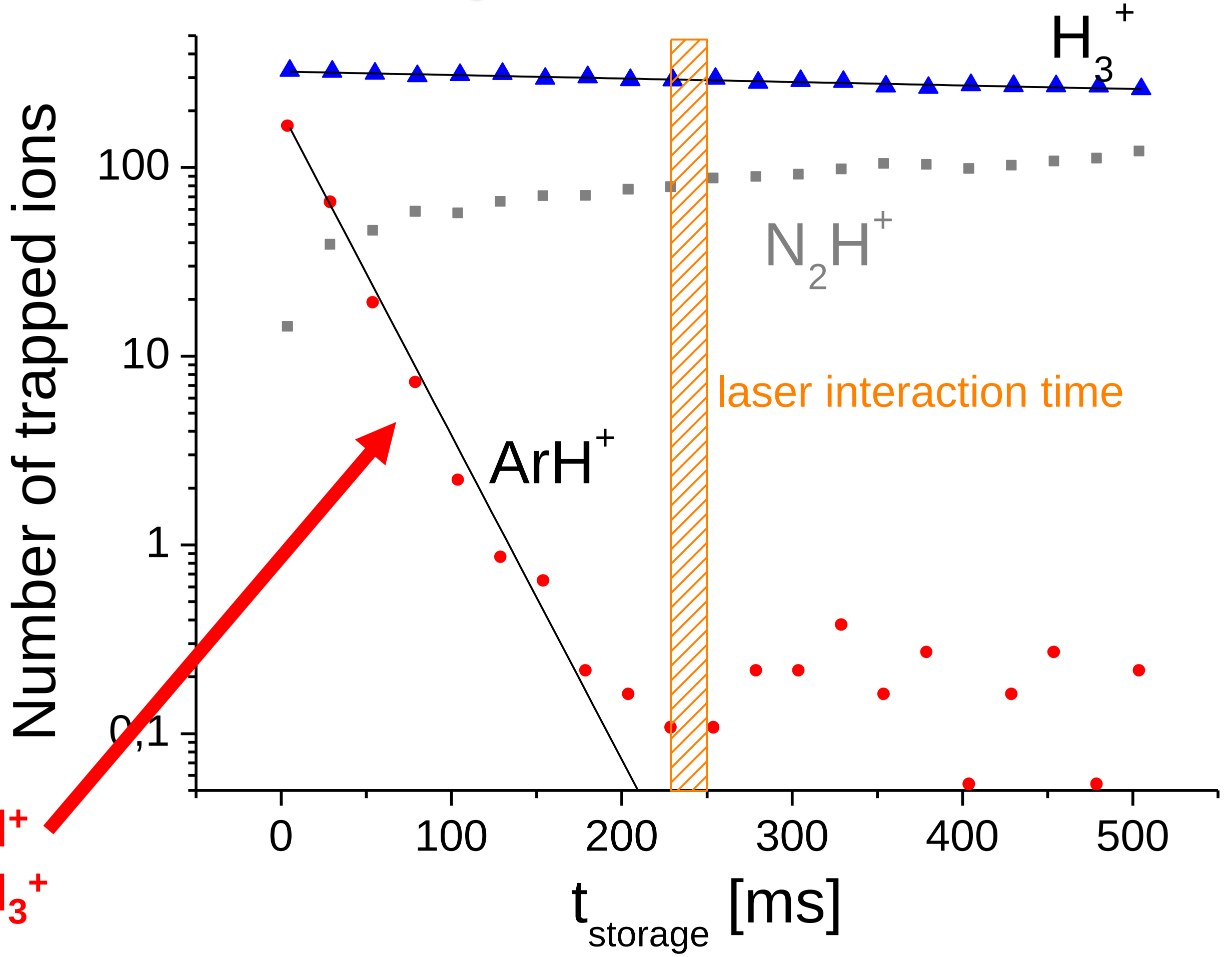
$H_3^+ (v_2=3) + Ar \rightleftarrows ArH^+ + H_2$ (+ 0.30 eV)

Count ArH^+ products!

Spectroscopy of H_3^+ by laser-induced reactions

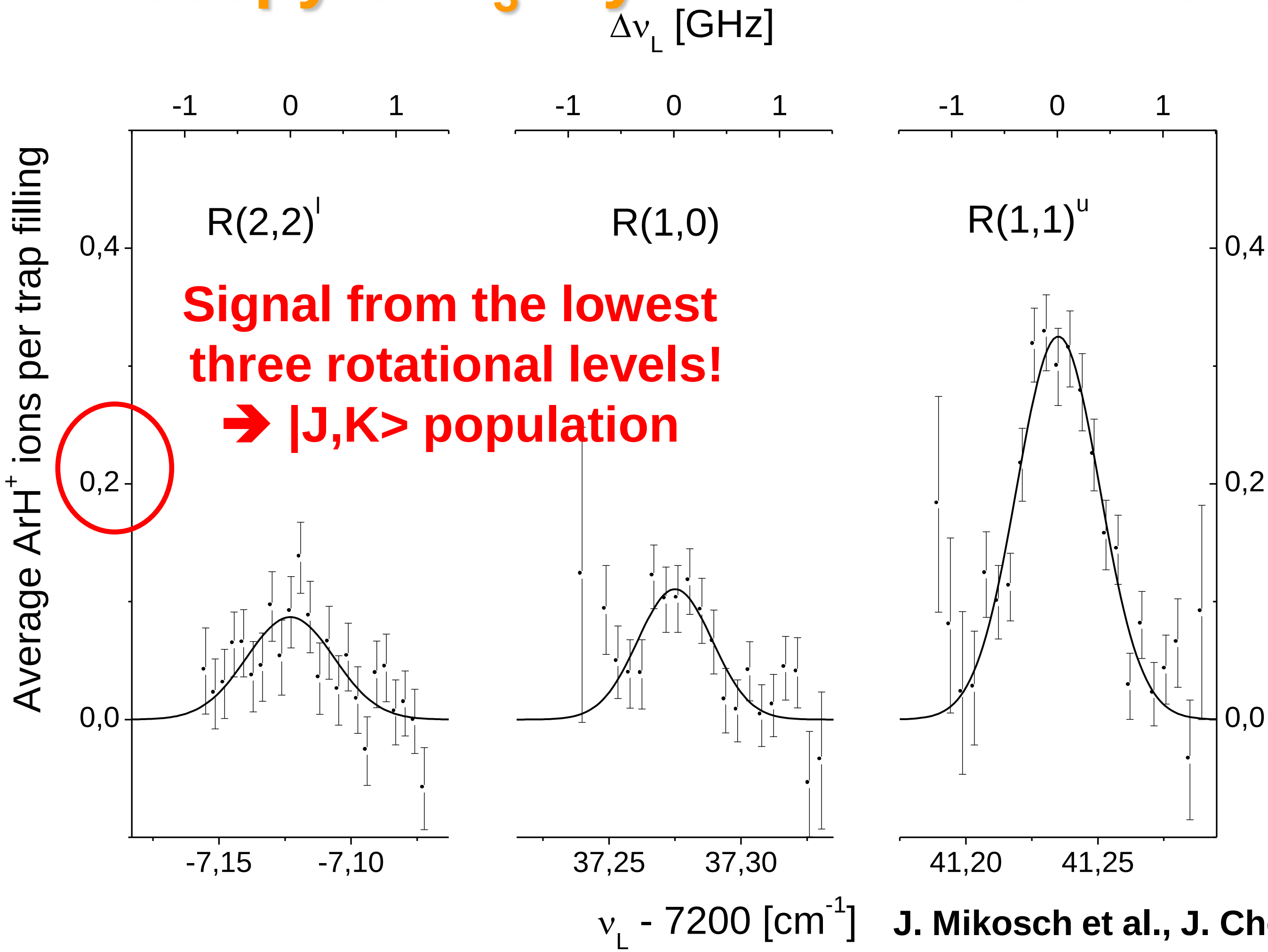


Spectroscopy of H_3^+ by laser-induced reactions



Initial ArH^+ from hot H_3^+

Spectroscopy of H_3^+ by laser-induced reactions

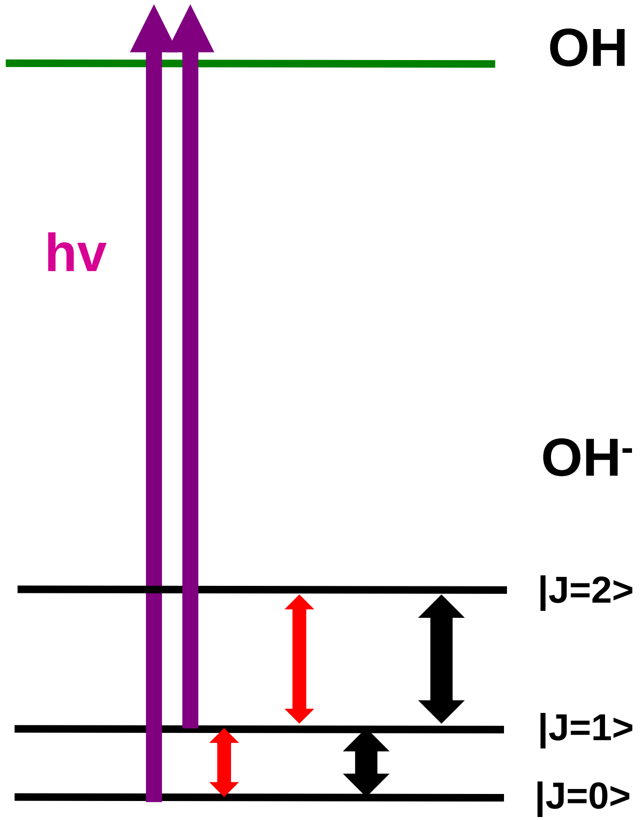


J. Mikosch et al., J. Chem. Phys. (2004)

Outline

- ❖ Spectroscopy in multipole rf ion traps
- ❖ Vibrational overtone transitions
- ❖ **Bound-free photodetachment spectroscopy**
- ❖ **Terahertz rotational spectroscopy**
- ❖ Electronic spectra of the Atkins‘ snowball

Rotational transitions in cold OH^-



Couplings between rotational states:

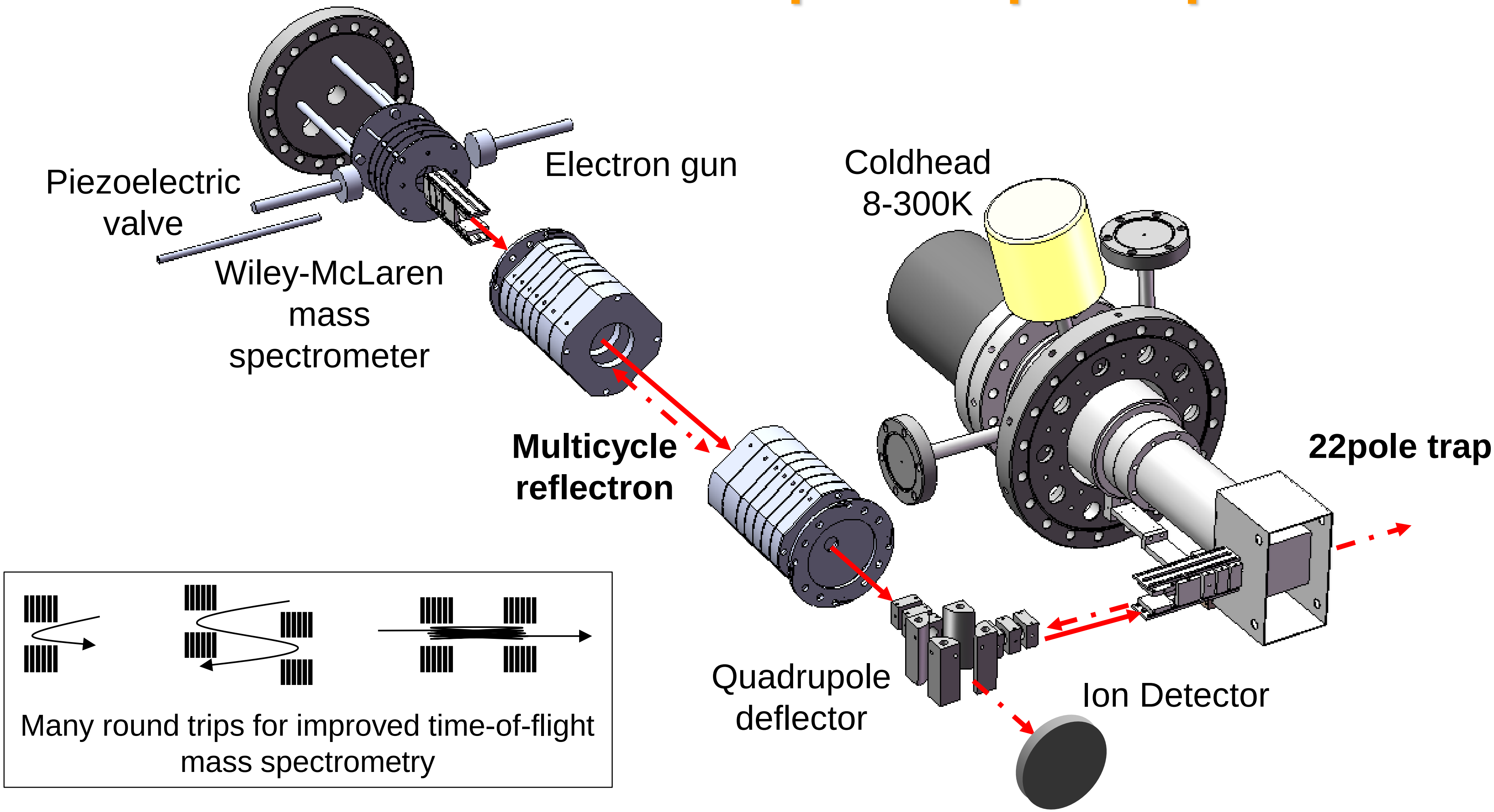
- **Collisions with helium buffer gas**
- **Terahertz rotational transitions**

Photodetachment as probe of J

$$OH^- + h\nu \rightarrow OH + e^-$$

ΔE = 37.5cm^{-1} or 54 K

The Innsbruck 22-pole trap setup

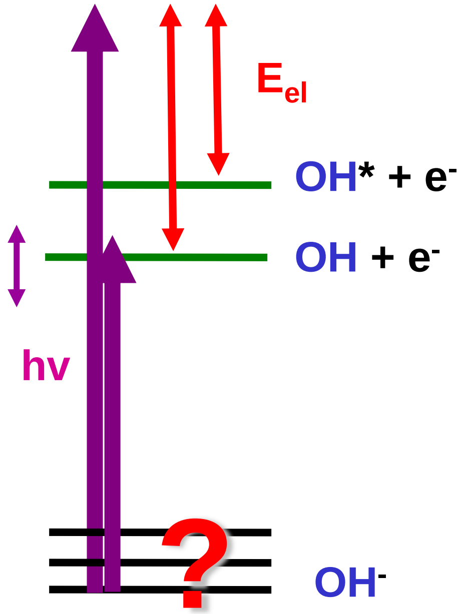


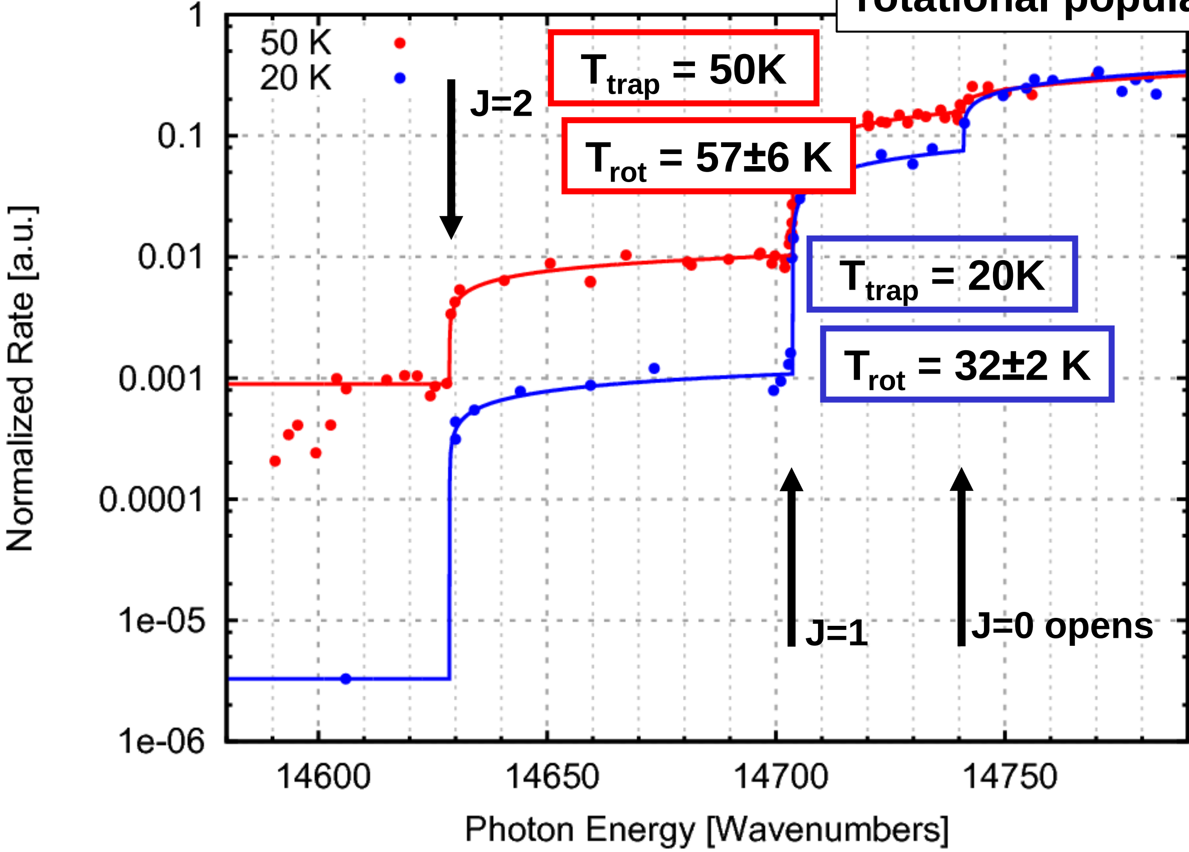
Many round trips for improved time-of-flight mass spectrometry

Photodetachment spectroscopy of cold OH^-

$OH^- + h\nu@680nm \rightarrow OH + e^-$

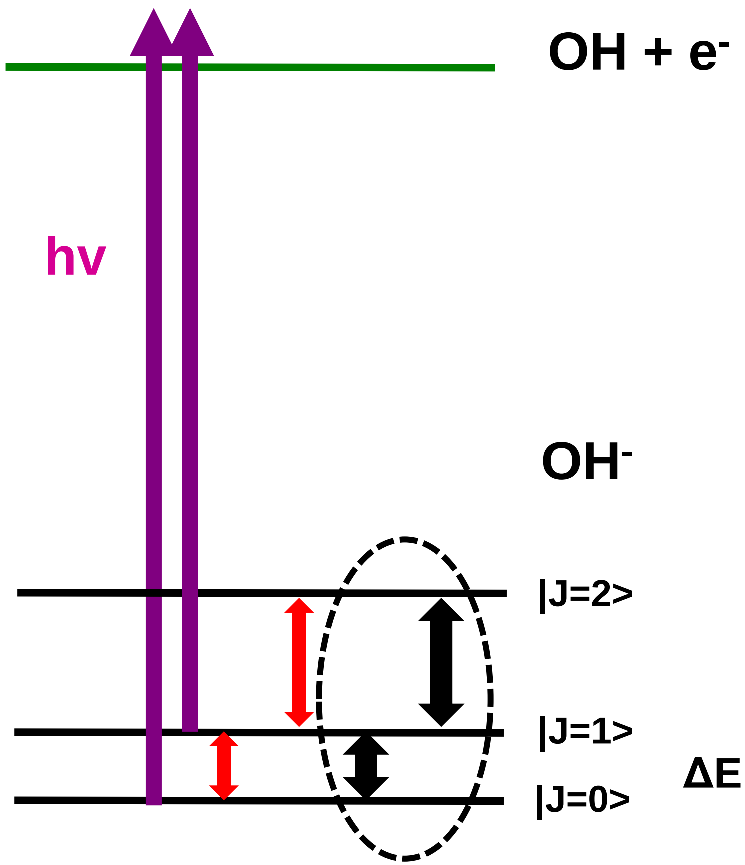
Plateau heights yield rotational populations





R. Otto *et al.*, PCCP (2013)

Rotational transitions in cold OH^-



Couplings between rotational states:

- Collisions with helium buffer gas
- Terahertz rotational transitions

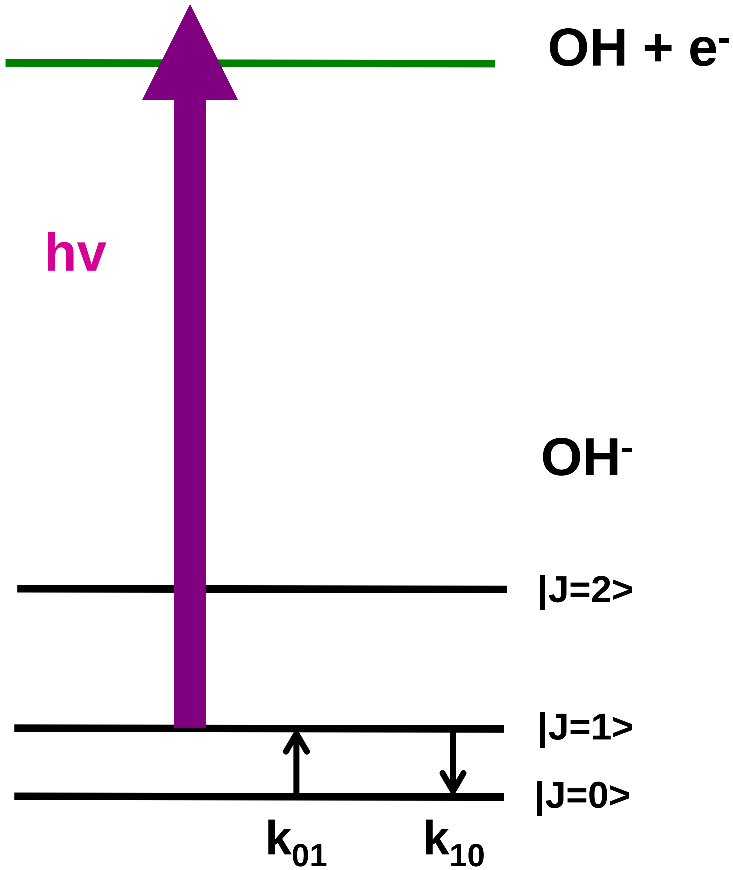
Photodetachment as probe of J

$OH^- + h\nu \rightarrow OH + e^-$

$\Delta E = 37.5\,\mathrm{cm}^{-1}$ or 54 K

Rotational transitions in cold OH^-

Photodetachment with *strong* laser



$$\frac{d}{dt}N_0 = -\,k_{01}\cdot N_0 + k_{10}\cdot N_1$$

$$\frac{d}{dt}N_1 = +\,k_{01}\cdot N_0 - [k_{10} + k_{PD}]\cdot N_1$$

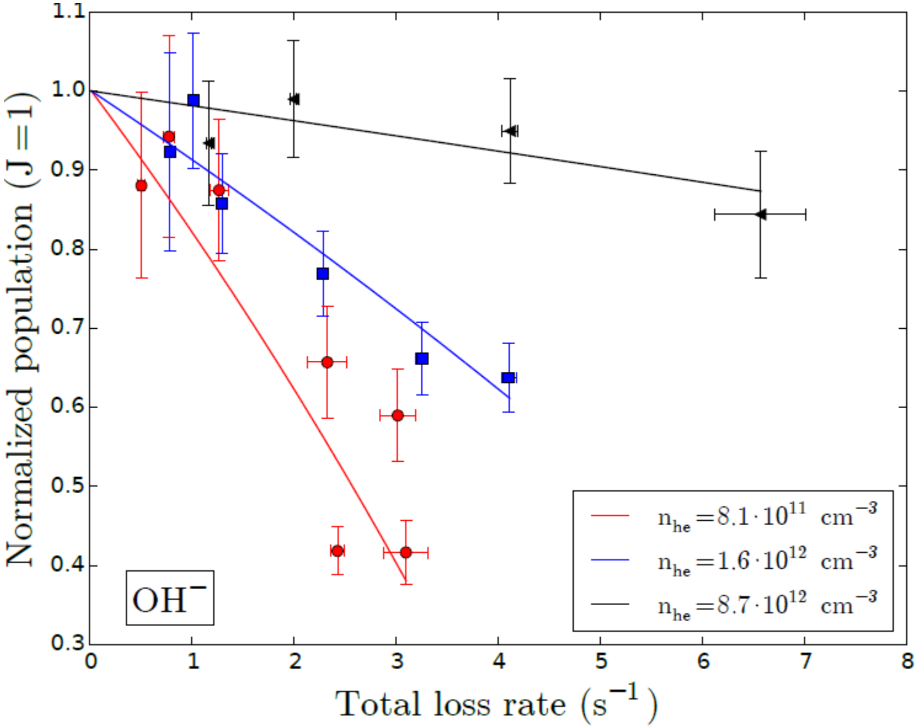
➔ **Laser depletion of excited state yields inelastic collision rate**

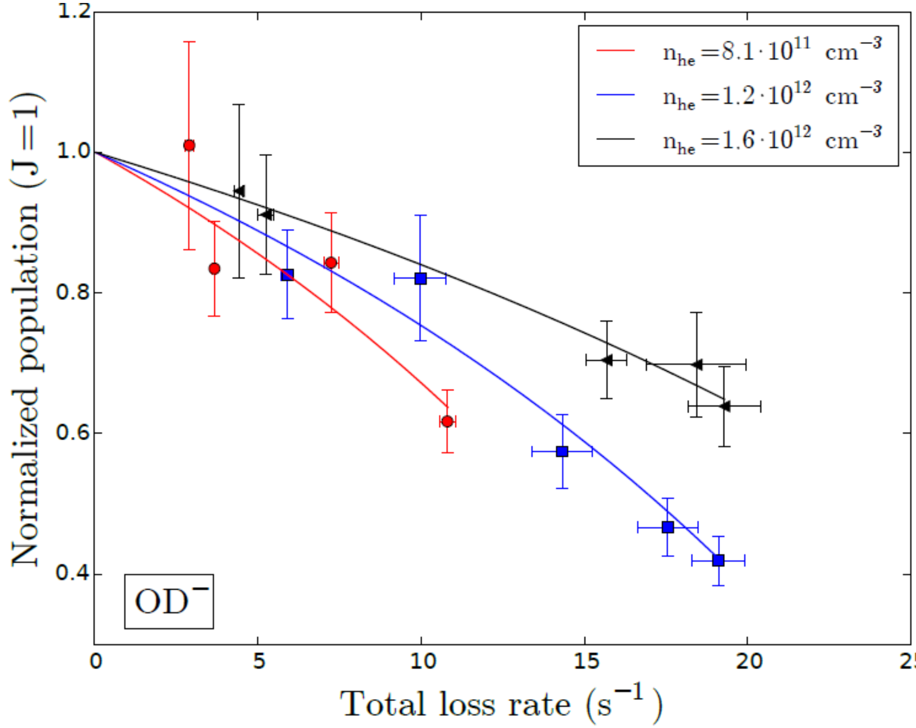
k_{10}, k_{01}: helium inelastic collision rates

OH⁻ rotational quenching: J=1→0

Changing the rotational state population

Ion collision temperature: 22 K





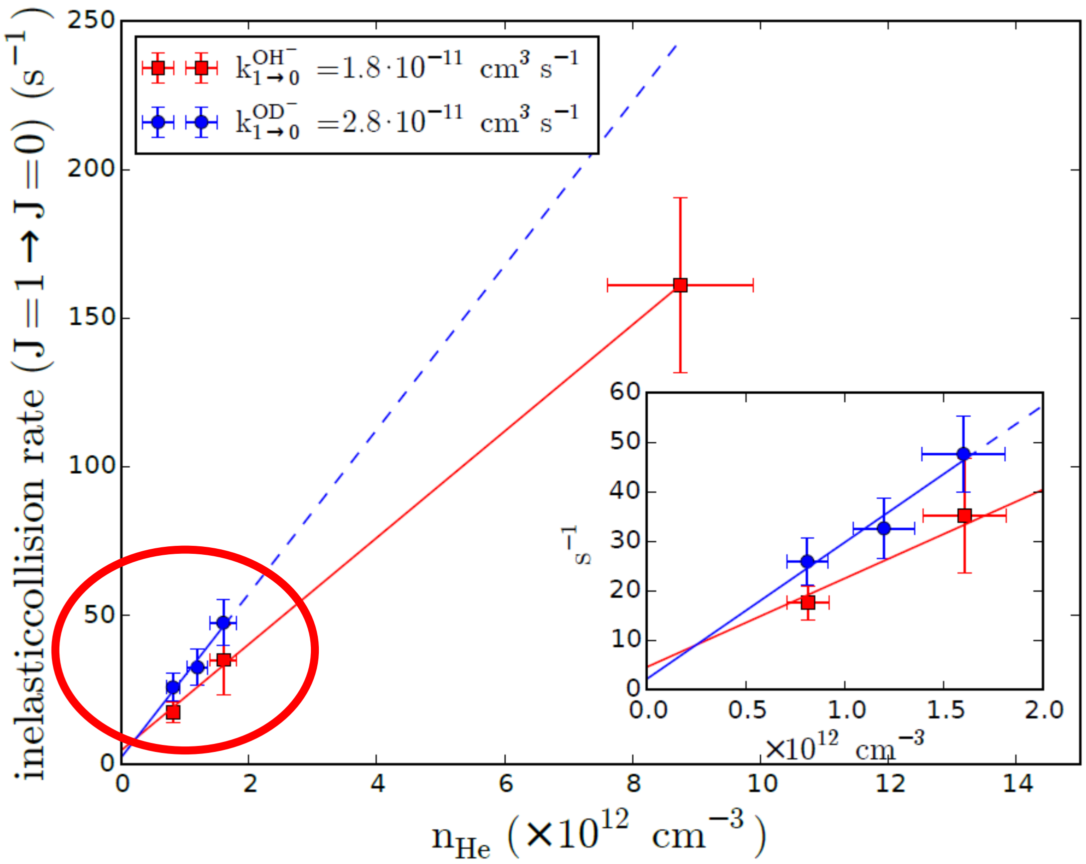
Faster detachment rate ➔ stronger depletion of J=1

Fit: model with inelastic collision rate k_{01} as only free parameter

OH⁻ rotational quenching: J=1→0

Density dependent inelastic rates

Ion collision temperature: 22 K



Slope: absolute inelastic rate coefficient

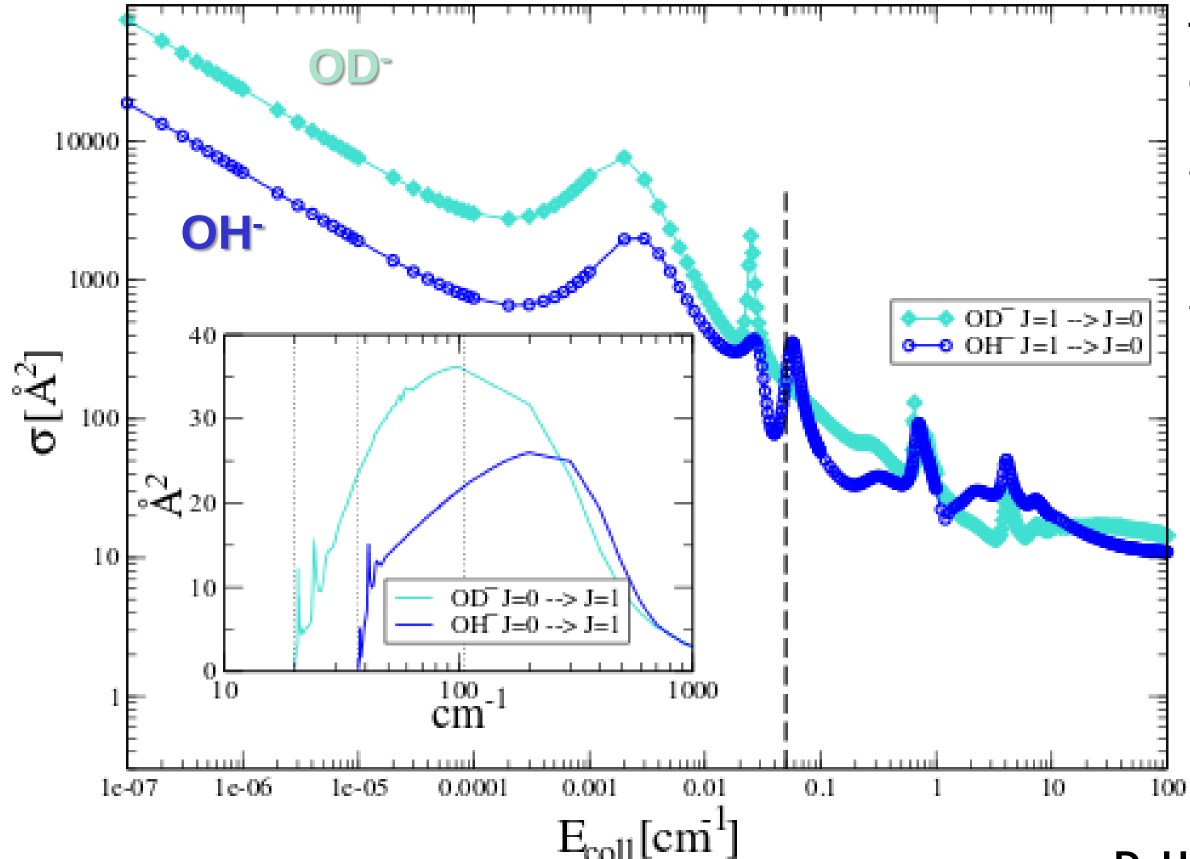
OH⁻ :
$k_{J=1\to 0} = (1.8 \pm 0.4_{stat} \pm 0.2_{syst}) \times 10^{-11}$ cm^3/s

OD⁻:
$k_{J=1\to 0} = (2.8 \pm 1.1_{stat} \pm 0.4_{syst}) \times 10^{-11}$ cm^3/s

D. Hauser *et al.*, Nature Physics (2015)

OH^- / OD^- rotational quenching: J=1→0

Quantum scattering calculations



Time-independent quantum coupled-channel calculations

- **Full Born-Oppenheimer surface, identical for OH^- and OD^- MP4/aug-cc-pVQZ**
- **Partial waves up to 40ħ**

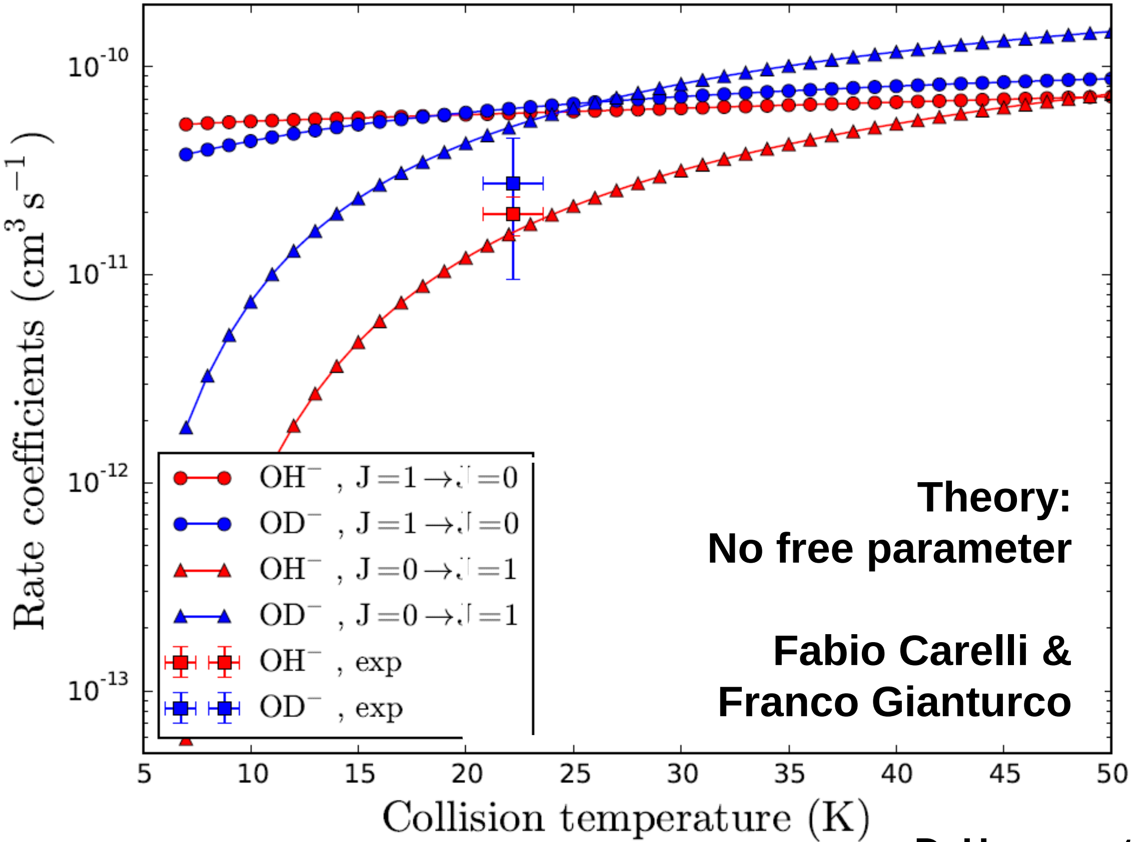
➔ Substantial differences for OH^- and OD^-

Fabio Carelli & Franco Gianturco

D. Hauser *et al.*, Nature Physics (2015)

OH^- rotational quenching: J=1→0

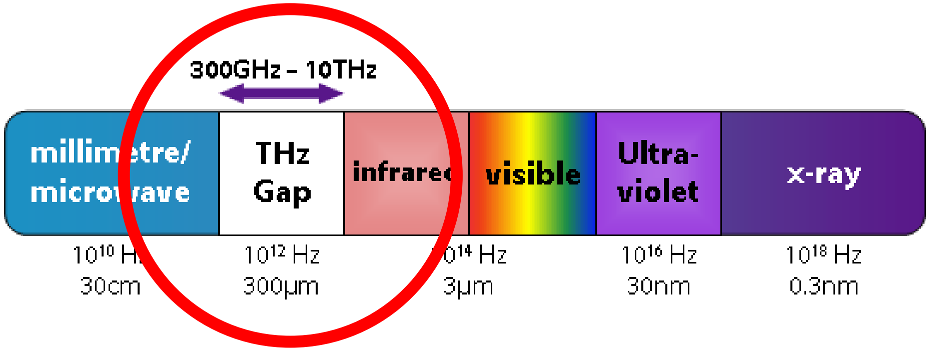
Thermal inelastic rate coefficients

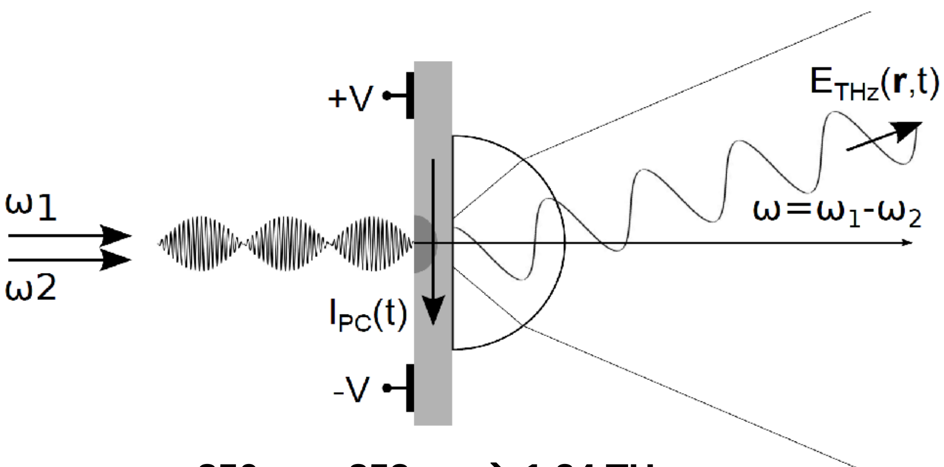


D. Hauser *et al.*, Nature Physics (2015)

Direct OH^- rotational excitation

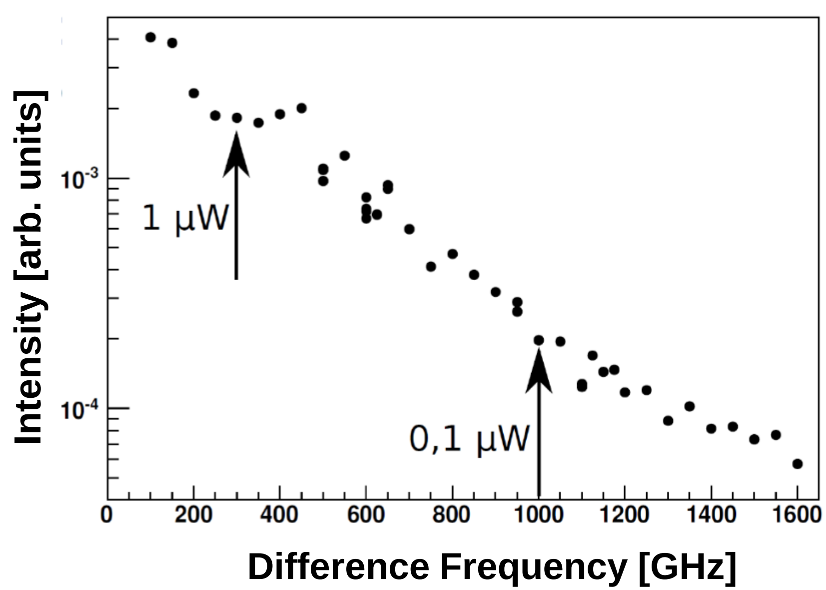
Terahertz spectroscopy with difference frequency mixing





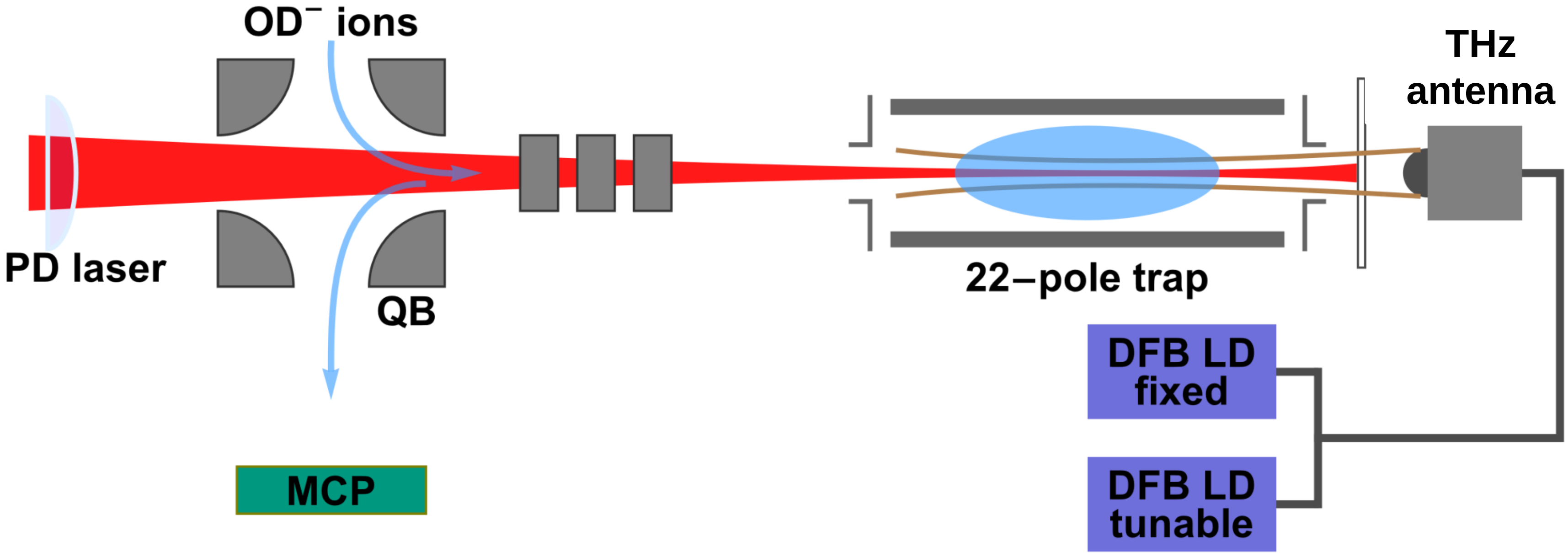
850nm - 853nm → 1.24 THz

Antenna output power



Direct OH^- rotational excitation

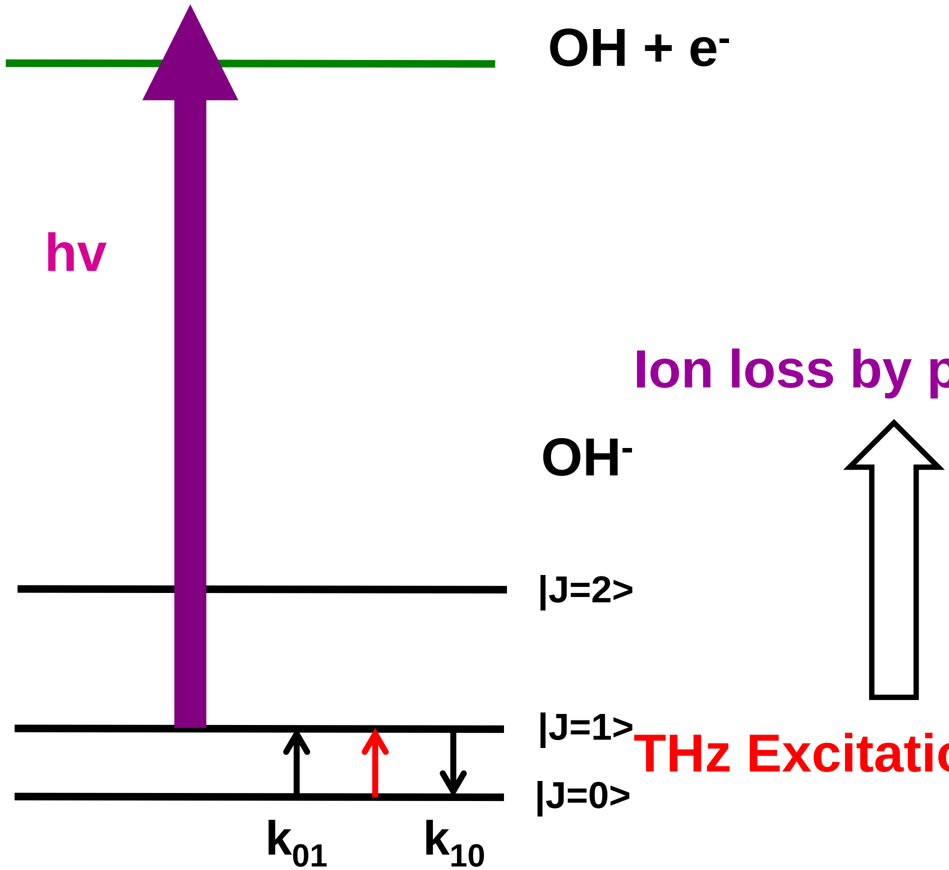
Bringing the THz antenna close to the ion trap



Direct OH^{-} rotational excitation

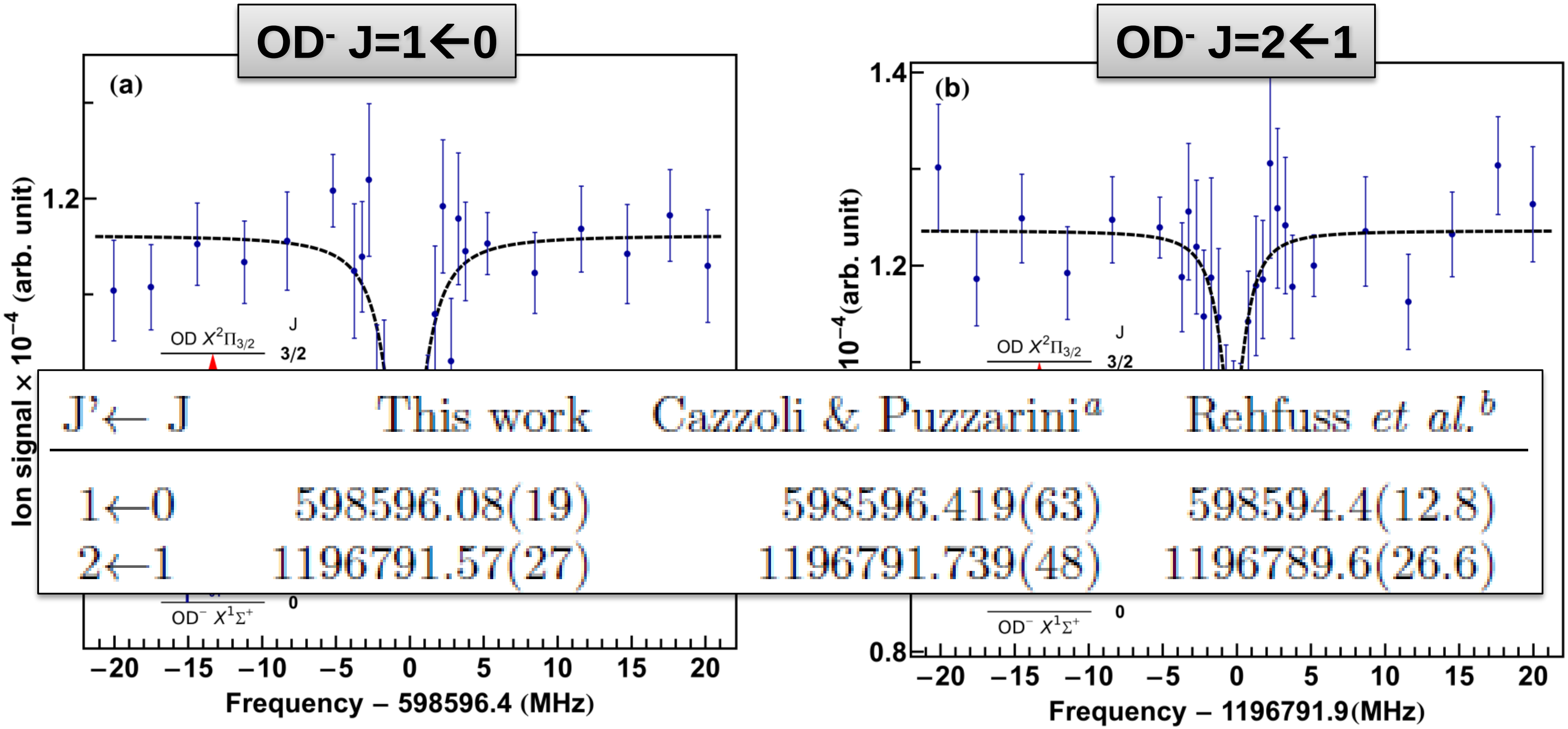
Terahertz spectroscopy via photodetachment

Important:
Low rates for collisional excitation/deexcitation



Direct OH^- rotational excitation

Terahertz spectroscopy via photodetachment



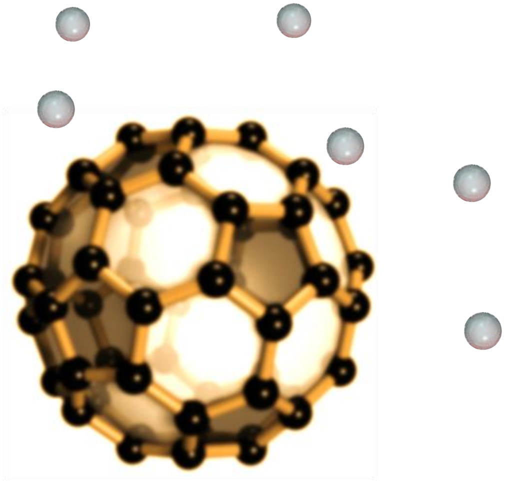
J'← J	This work	Cazzoli & Puzzarini[a]	Rehfuss *et al.*[b]
1←0	598596.08(19)	598596.419(63)	598594.4(12.8)
2←1	1196791.57(27)	1196791.739(48)	1196789.6(26.6)

Outline

- ❖ Spectroscopy in multipole rf ion traps
- ❖ Vibrational overtone transitions
- ❖ Bound-free photodetachment spectroscopy
- ❖ Terahertz rotational spectroscopy
- ❖ **Electronic spectra of the Atkins‘ snowball**

Electronic spectra of an Atkins‘ snowball

(an experiment without an ion trap)



$C_{60}^{+}(He)_n$

THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 116, NO. 6 DECEMBER 15, 1959

Ions in Liquid Helium*

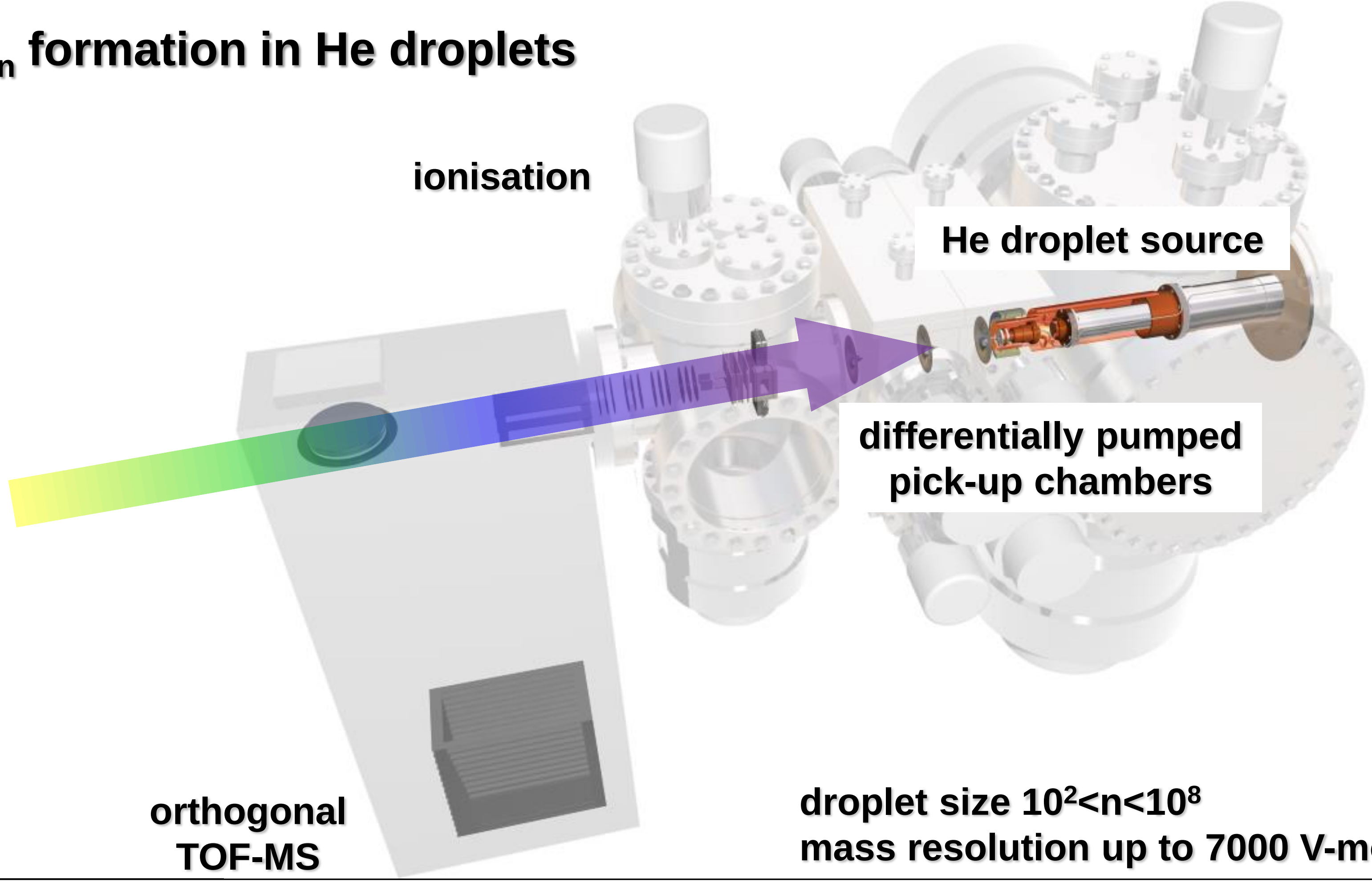
K. R. ATKINS
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania

(Received July 16, 1959; revised manuscript received September 30, 1959)

H. Linnartz, X. Tielens, J. Cami, A. Y. Wang, M. Alcamí, F. Martín, M. Beyer, RW, A. Lindinger, *et al.*
P. Scheier

Electronic spectra of an Atkins' snowball

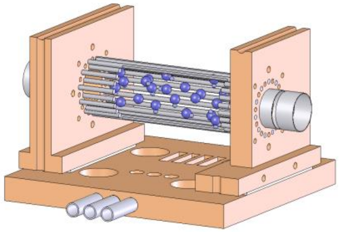
$C_{60}^{+}(He)_n$ formation in He droplets



droplet size $10^2 < n < 10^8$

mass resolution up to 7000 V-mode

Summary



Spectroscopy in ion traps by laser-induced reactions

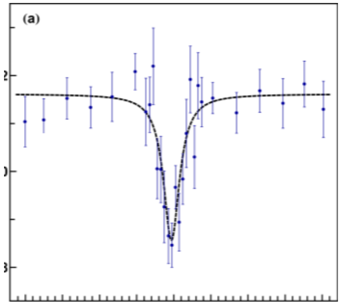
:: Vibrational spectroscopy of H_3^+ overtones

Rotational spectroscopy of trapped ions

:: Near-threshold detachment for OH^- → rotational populations

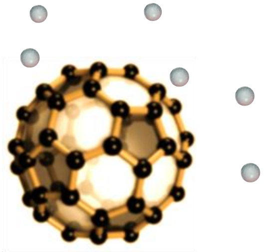
:: Cold state-to-state inelastic rate coefficients

:: Rotational excitation by direct THz absorption

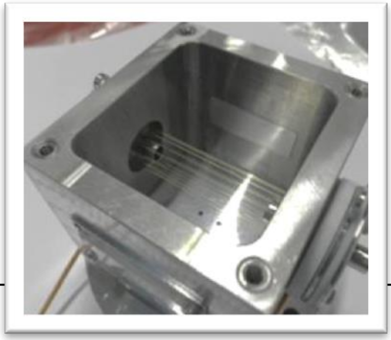


Electronic spectra in He droplets

:: Line shifts of $C_{60}^+(He)_n$ Atkins snowball
reveal phase transitions



Outlook



:: THz spectroscopy of polyatomic ions

:: Dipole-bound states in carbon chain ions

:: Inelastic collision rates for open-shell ions

Thank you

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